FIXED BED ADSORPTION OF CARBON DIOXIDE ON MODIFIED COCONUT SHELL GRANULAR ACTIVATED CARBON

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by

TAN YEE LING

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LIST OF SYMBOLS

Symbol	Description	Unit
Å	Angstrom	Å
C_0 or c_F	Initial CO_2 concentration	vol%
C_{eff}	Effluent CO_2 concentration	mg/mL
C_{in}	Inffluent CO_2 concentration	mg/mL
L	Column length	m
P	Pressure	bar
P_0	Initial pressure	bar
Q	Gas flow rate	mL/min
q	Adsorption capacity	mg/g or mmol/g
T	Adsorption temperature	°C or K
t	Contact time	min
ε	Bed porosity	-
τ	Breakthrough time	s
υ	Superficial velocity	m/s

LIST OF ABBREVIATIONS

AA	Activated alumina
AC	Activated carbon
APTES	(3-aminopropyl) triethoxysilane
BDDT	Brunauer, Deming, Deming and Teller
BET	Brunauer-Emmett-Teller
CCS	Carbon dioxide capture, utilization and storage
EIA	US Energy Information Administration
FT-IR	Fourier Transform Infrared
IPCC	Intergovernmental Panel on Climate Change
IUPAC	International Union of Pure and Applied Chemistry
NaOH	Sodium hydroxide
NASA	National Aeronautics and Space Administration
NOAA	National Oceanic and Atmospheric Administration
PEI	Polyethylenimine
SEM	Scanning Electron Microscopy
TEA	Triethanolamine
TVSA	Temperature/vacuum swing adsorption
vol%	Volume percentage
wt%	Weight percentage

PENJERAPAN LAPISAN TETAP KARBON DIOKSIDA KE ATAS KARBON TERAKTIF TEMPURUNG KELAPA TERUBAHSUAI

ABSTRAK

Penjerap diubahsuai secara kimia telah menarik perhatian atas keupayaannya menangkap karbon dioksida untuk meningkatkan kapasiti penjerapan dan ciri-cirinya seperti rintangan haba dan kimia. Dalam kajian ini, satu siri karbon teraktif tempurung kelapa terubahsuai telah disediakan, dicirikan dan digunakan dalam proses penjerapan CO_2 dalam sistem penjerapan lapisan tetap. Karbon teraktif granula tempurung kelapa dipilih disebabkan luas permukaannya yang tinggi, ciri kestabilannya untuk menahan kerosakan di bawah kitaran pemanasan dan kos yang rendah di kalangan penjerap yang sedia ada dalam pasaran. Bahan kimia beralkali seperti trietanolamina (TEA), natrium hidroksida (NaOH), kitosan, 3-aminopropil-trietoksisilana (APTES) dan polietalinimina (PEI) telah digunakan untuk mengubah suai karbon teraktif. Dua kaedah penyediaan telah diguna, kaedah impregnasi dan manik kitosan oleh penjelan alkali. Sifat-sifat permukaan, kumpulan berfungsi dan morfologi permukaan penjerap yang disediakan telah dicirikan oleh BET, FT-IR dan SEM, masing-masing. Penjerapan karbon dioksida telah dijalankan dalam sistem penjerapan lapisan tetap dengan penganalisis karbon dioksida dalam masa nyata untuk menentukan kepekatan karbon dioksida dalam gas keluar. Kesan-kesan keadaan operasi seperti kadar aliran gas (90-150 mL/min), suhu penjerapan (35-55 °C), muatan penjerap (bergantung kepada ketumpatan bahan penjerap) dan kepekatan asal CO_2 (10-20%) telah dikaji. Keputusan BET menunjukkan bahawa luas permukaan menurun dan ciri-ciri liang berubah selepas pengubahsuaian secara

kimia. FT-IR spektra bagi sampel yang tidak diubahsuai dan yang terubahsuai adalah sama disebabkan dos bahan kimia yang sedikit pada karbon teraktif terimpregnasi. Kapasiti penjerapan lapisan karbon teraktif yang tidak diubahsuai adalah 17.52 mg/g dengan muatan penjerap 3 g, suhu penjerapan 35 °C, kadar aliran gas 90 mL/min dan 10% CO_2. Kapasiti penjerapan tertinggi adalah 81.56 mg/g, telah diperolehi dengan menggunakan manik kitosan-PEI-AC dengan muatan penjerap 0.5 g, suhu penjerapan 35 °C, kadar aliran gas 90 mL/min dan 10% CO_2. Sampel terubahsuai dengan kestabilan yang terbaik dalam ujian kitaran adalah 125CAC6 dengan kemerosotan sebanyak 11.30% ke atas 10 proses kitaran penjerapan. Keputusan kajian menunjukkan bahawa pengubahsuaian secara kimia pada karbon teraktif memberi kesan positif kepada prestasi penjerapan.

FIXED BED ADSORPTION OF CARBON DIOXIDE ON MODIFIED COCONUT SHELL GRANULAR ACTIVATED CARBON

ABSTRACT

Chemically modified adsorbent is attracting attention on its ability in carbon dioxide capture in order to increase the adsorption capacity and enhance its characteristics such as thermal and chemical resistance. In this research, a series of chemically modified coconut shell granular activated carbon were prepared, characterized and used in CO_2 adsorption process in a fixed-bed adsorption system. Coconut shell granular activated carbon was chosen due to its large surface area, its stable properties to withstand destruct under cyclic heating and relatively low cost among the adsorbents available in the market. Basic chemicals such as triethanolamine (TEA), sodium hydroxide (NaOH), chitosan, 3-aminopropyl-triethoxysilane (APTES) and polyethylenimine (PEI) were used to modify the activated carbon. Two preparation methods were used, the impregnation method and chitosan beads preparation method by alkali gelation. The surface properties, functional groups and surface morphologies of the prepared adsorbents were characterized by BET, FT-IR and SEM, respectively. The adsorption of carbon dioxide was carried out in a fixed bed adsorption system with an online carbon dioxide analyzer to determine the concentration of carbon dioxide in the outlet gas. The effect of operating conditions such as gas flow rate (90-150 mL/min), adsorption temperature (35-55 °C), adsorbent loading (depends on the density of adsorbent) and initial CO_2 concentration (10-20%) were studied. The BET results showed that the surface area decreased and the pore characteristics changed after chemical modification. The FT-IR spectra of the

unmodified and modified samples were similar due to a small dosage of chemicals was impregnated onto the activated carbon. The bed adsorption capacity of unmodified activated carbon was 17.52 mg/g with adsorbent loading 3 g, adsorption temperature 35 °C, gas flow rate 90 mL/min and 10% CO_2. The highest adsorption capacity was 81.56 mg/g, which was obtained by using chitosan-PEI-AC beads with adsorbent loading of 0.5 g, adsorption temperature 35 °C, gas flow rate 90 mL/min and 10% CO_2. The modified sample with the best stability in the regeneration test was 125CAC6, which decreased about 11.30% over 10 cyclic adsorption process. The results showed that chemical modification of activated carbon gave positive effects on the adsorption performance.

CHAPTER ONE

INTRODUCTION

Climate change is changing our economy, health, and communities in diverse ways (IPCC, 2007). The prospect of a worsening climatic situation due to global warming results from the emission of greenhouse gases has received widespread attention. A layer of greenhouse gases, which consists of greenhouse gases such as water vapour, carbon dioxide, methane and nitrous oxide, acts as a thermal blanket around the Earth (IPCC, 2007). It absorbed and trapped the heat that reflected back from Earth to space and keep the Earth "warming". Thus, the local temperatures are fluctuating and the average global temperature has increased over the past 50 years. The United State Global Research Program stated that "global warming is unequivocal and primarily human-induced" and "climate changes are underway in the United States and are projected to grow" (Karl et al., 2009). These statements show that the global warming is mainly due to the human activities. Thus, we must find out an effective way to address this problem.

Carbon dioxide (CO_2) is one of the greenhouse gases that can be released by respiration or human activities such as fossil fuel burning and contributes more than 60% to global warming because of its huge emission amount. Concerns over the gradual increase in atmospheric concentration of CO_2 and its impact on climate change have prompted a global research effort to capture the carbon dioxide gas from point source emissions and stabilize its concentration in the atmosphere (Shafeeyan et al., 2010). According to National Aeronautics and Space Administration (NASA) and National Oceanic and Atmospheric Administration (NOAA) from United State,

the concentration of CO_2 had been increased drastically from 280 ppm to a new record of 400 ppm since the Industrial Revolution in 18^{th} century in Europe (Showstack, 2013). Copenhagen Accord also requests the global temperature increase be limited to 2 °C above the pre-industrial level by the year 2100. The upper safety limit of atmospheric CO_2 concentration should be 350 ppm but unfortunately the atmospheric CO_2 concentration has been beyond this limit since year 1988. Since CO_2 is a long-lived gas, which does not respond physically or chemically when it shields the Earth, it is necessary to find a mitigation action to reduce carbon dioxide emissions (Pires et al., 2011).

The urgent need for strategies to reduce global atmospheric concentration of CO_2 has prompted action from all over the world. There are numerous reports and comprehensive articles have considered the engineering feasibility and economics of CO_2 capture (Kim et al., 2010; Sun et al., 2013; Silva et al., 2014). Three CO_2 separations are considered to hold the greatest promise for reducing CO_2 emission, which are: separation from power plant flue gas, separation from sour natural gas well, and separation from fuel gas. The schematic diagram of CO_2 separation from natural gas is shown in Figure 1.1 while the schematic diagram of CO_2 capture from industrial processes is shown in Figure 1.2.

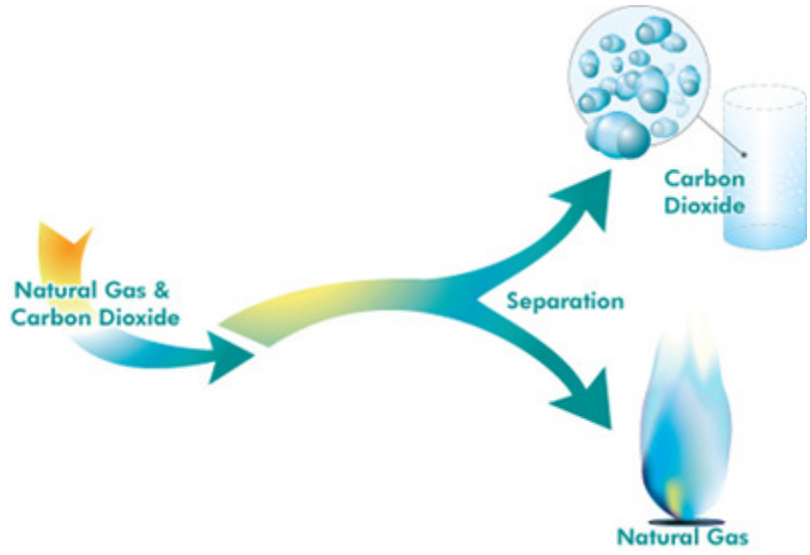

Figure 1.1: CO_2 separation from natural gas (CO2CRC, 2011).

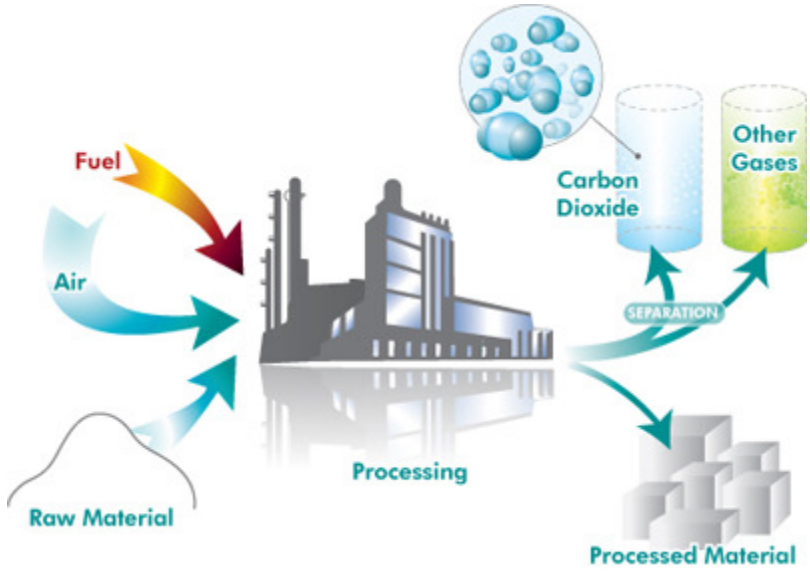

Figure 1.2: CO_2 separation from industrial processes (CO2CRC, 2011).

As a result of the industrial growth, there is an approximately 7 Gt of carbon emitted to the atmosphere annually, mainly in the gaseous form of CO_2 (Siegenthaler & Sarmiento, 1993). Among these carbon emissions, about 30% of the CO_2 are released from fossil fuel power plant (Figure 1.3). The major obstacle of CO_2 capture in the separation from flue gas is the low pressure and low CO_2 concentration. Flue gases from combustion facilities have a composition different from the air due to the

high concentrations of H_2O and CO_2 (Wall et al., 2009). For example, the main components of the flue gas from pulverized coal combustion are CO_2, N_2, O_2 and H_2O, air pollutants such as SO_x, NO_x, particulates, HCl, HF and mercury, as well as other contaminants.

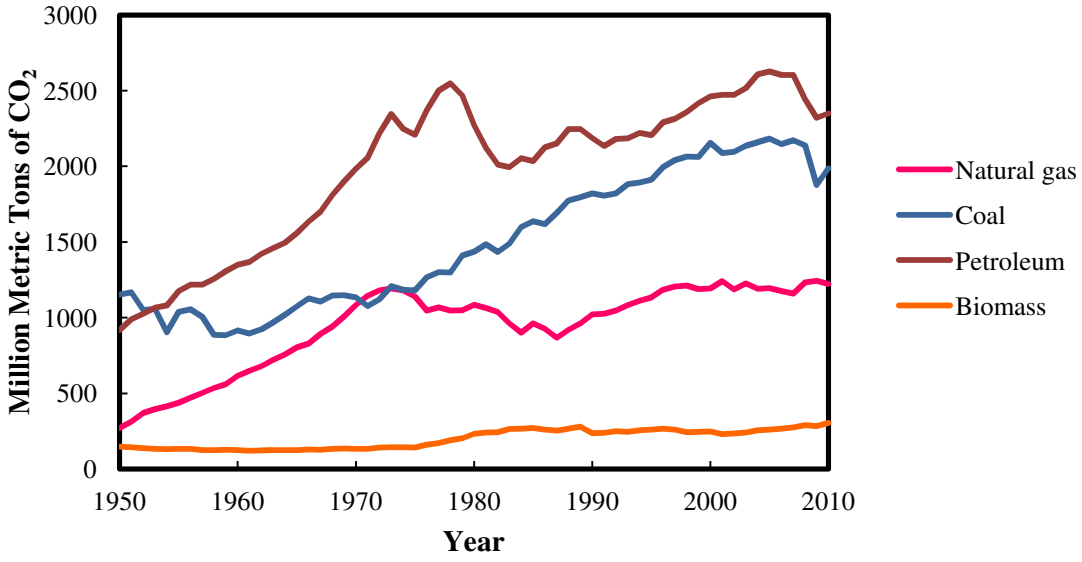

Figure 1.3: CO_2 emissions from fossil fuel power plants over the past 6 decades (EIA, 2011).

The increasing of international energy demand shows a 1.7% average annual growth in the 2005-2020 period. There are some energy sources are under developing such as nuclear and solar energy to substitute the use of fossil fuel, but fossil fuels still rule the energy scene for these years. Natural gas is another substitute for coal, which is a conventional energy source that brings many pollution issues. According to Malaysia Petroleum Resources Corporation, Malaysia has some 28.35 billion barrels of oil reserves and about 1.2% of the world's natural gas reserves (2.34 trillion m^3) of proven reserves. US Energy Information Administration (EIA) also states that Malaysia is the second largest oil and natural gas producer in

Southeast Asia, the second largest exporter of liquefied natural gas globally after Qatar, and is strategically located amid important routes for seaborne energy trade. Natural gas is not only used as a source of energy, but it is also widely used in the pertrochemical industry as a raw material. For natural gas treating technologies, it can be separated into two categories, which are separation (with 10% or higher of contaminant in feed) and purification (with less than 3% of contaminant in feed). The CO_2 separation from natural gas is usually done at high temperatures (250-450 °C) and under high pressure from the gas wells (normally between 2030 and 7090 kPa).

The key challenges for gas separation materials is to find a suitable material with good capture capacity and selectivity. There are many ways to capture CO_2 (Figure 1.4) such as adsorption, absorption and membrane diffusion. The principles of separation of these methods are different and thus the materials applied also vary. For example, absorption involves the capture of CO_2 by liquid amine such as monoethanolamine and triethanolamine; adsorption involves the capture of CO_2 by solid adsorbent such as zeolite, silica and activated carbon; and membrane diffusion separate CO_2 from the flue gas with the characteristics of membrane especially the gas permeability and selectivity.

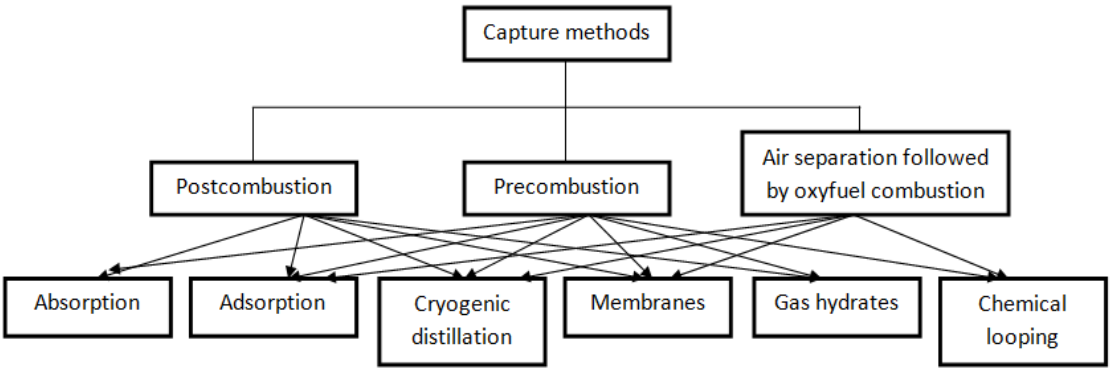

Figure 1.4: Overview of CO_2 capture technologies (Kenarsari et al., 2013).

Among these three methods, absorption process has been commonly practiced in the industry for over 50 years. This process involves the passage of aqueous MEA solution with concentration around 25-30wt% down the top of absorption tower, while the flue gas is introduced at bottom. The reaction between CO_2 and amine occurs through a zwitterion mechanism to form carbamate at temperature 40 °C. The liquid with absorbed CO_2 will flow from the absorber column to the stripping tower and heated with steam to regenerate CO_2. The advantage of this separation process is that the regeneration process can be done at elevated temperature (100-140 °C) and pressures slightly higher than the atmospheric pressure. After that, the liquid amine solution can be recycled and used for the next absorption process. However, there are some drawbacks that forcing the scientists to find an alternative way for it, such as corrosion of absorption column and reduction of efficiency.

Adsorption process can be used as the alternate for amine scrubbing where the adsorption capacity is mainly affected by the surface area of the adsorbents. Nowadays, many researches and studies had been done in order to increase the adsorption capacity of the adsorbent in different ways. For instance, increase the surface area or micropore volume in order to enhance the amount of active sites for CO_2 capture, or functionalize the surface of adsorbent to increase the selectivity and also the adsorption capacity of that adsorbent.

1.1 Problem statement

The growth of industrial development is important for the economy of a country, but the side effect of rapid industrialization should not be neglected. Proper

waste management should be applied by each plant to prevent the harms towards the environment and also human health. Numerous methods had been studied to capture the CO_2 to prevent excess emission to the atmosphere.

The conventional absorption method by using alkanolamine can capture the CO_2 effectively, but it also creates another disposal and corrosion problem. The application of membrane in CO_2 separation can successfully remove the CO_2 from the flue gas, but its cost is expensive and it is still under research. Adsorption can be the alternate for these methods because the disposal of adsorbent is relatively easier and safer, and the cost can be minimized by using some low-cost adsorbent such as zeolite and activated carbon. Activated carbon is widely used as CO_2 adsorbent due to its large surface area and low cost. However, its adsorption capacity per surface area is relatively low. Thus, surface modification is crucial to increase the affinity sites of activated carbon in order to increase its adsorption performance.

Chemical modification of adsorbent had been studied widely in order to minimize the production cost, increase the removal efficiency and enhance the selectivity. The chemicals which contain nitrogen groups are preferable in the modification of CO_2 adsorbents due to the Lewis acid-base interaction (Yin et al., 2007). Other than nitrogen-containing chemicals, basic chemical such as potassium hydroxide is also favoured in the modification of CO_2 adsorbents (Yong et al., 2002). Thus, different types of basic chemicals such as triethanolamine (TEA), sodium hydroxide (NaOH), chitosan, (3-aminopropyl)triethoxysilane (APTES) and polyethylenimine (PEI) were selected to modify the AC adsorbent.

1.2 Research objectives

This research study is aimed to enhance the adsorption performance of a commercial coconut shell activated carbon by chemical modification. The objectives were:

i. To modify the coconut shell AC with TEA, NaOH, chitosan, APTES and PEI with different chemical loading and contact time to obtain the sample with the best CO_2 adsorption performance.
ii. To characterize the modified adsorbents for physical and chemical properties in terms of surface morphology, surface area, pore size, pore volume and Fourier Transform Infrared spectrometry.
iii. To establish the breakthrough curves by studying the adsorption process parameters such as gas flow rate, adsorption temperature, adsorbent loading, initial concentration of CO_2 and the reusability of the modified adsorbents.

1.3 Scope of study

The scope of study of this study includes the modification, characterization, study of adsorption process parameters and regeneration of the modified adsorbents in the CO_2 adsorption using a fixed-bed adsorption system. Commercially available coconut shell AC was selected to be used as the support adsorbent in this study due to its good performance in adsorption and its stable properties. The commercial AC was modified by impregnation with TEA and NaOH solution with different dosages. The addition of TEA and NaOH are to enhance the basic sites of the adsorbents. Chitosan-AC beads was prepared by the alkali gelation. In general, chitosan bead was prepared by dissolving the chitosan in acetic acid solution to form a viscous

solution, and followed by dropwise addition of the chitosan solution to a solution of NaOH. Solid beads were formed due to the polymer precipitation. In this study, AC powder was added into the chitosan solution as the adsorbent while the role of chitosan is a nitrogen functional groups provider. In order to further enhance the basic sites in the adsorbent, APTES and PEI were selected to add into the chitosan-AC solution. Different parameters were studied to establish the best preparation method for the adsorbents such as chemical dosage and AC particle size to prepare bead.

The synthesized adsorbents were characterized by using SEM, BET and FT-IR analysis. The surface morphology, surface area, pore characteristic and functional groups of the fresh samples were determined. Futhermore, the functional groups of reused samples were characterized by FT-IR analysis to compare with the result of fresh samples.

A fabricated fixed-bed adsorption system with an online CO_2 analyzer was used to determine the CO_2 adsorption performance of the modified adsorbents. The effect of condition parameters such as gas flow rate, adsorption temperature, adsorbent loading, initial CO_2 concentration and the reusability were studied in order to obtain the best condition for CO_2 adsorption. Finally, the results will help to realize the CO_2 adsorption performance of the modified adsorbents and determine the optimum condition for CO_2 adsorption.

1.4 Organization of thesis

There are five chapters in this thesis:

Chapter one (Introduction) presents the current environmental issues and the brief description of CO_2 capture. It also provides the problem statement and the objectives of this research.

Chapter two (Literature reviews) describes the carbon dioxide capture and storage (CCS) technique, different methods to capture CO_2 and surface modification of adsorbents. The limitations of these methods are outlined. Different types of adsorbent had been discussed and their adsorption performances were compared. The effect of operating parameters using modified adsorbent was discussed.

Chapter three (Materials and methods) shows the outline of experimental works in this research. This chapter is divided into three parts. The materials, chemicals and equipments used are listed in the first and second part. In the third part, the methods of preparation for each adsorbent are described in details. The procedures for CO_2 adsorption study, regeneration and the calculations of adsorption capacity are also included in this part.

Chapter four (Results and discussion) presents all the results and discussions on the findings. This chapter is divided into parts. Part one shows the result of preliminary studies on commercial adsorbents with different sizes and their performances after modification. Part two is the results of characterization and part three shows the adsorption performances of modified samples with different preparation parameters. In part four, the effect of operating parameters on the adsorption performances are described. The results of regeneration is shown in part five.

Finally, chapter five (Conclusions and recommendations) summarizes the data reported and also gives some recommendations for future research.

CHAPTER TWO

LITERATURE REVIEW

2.1 Carbon dioxide capture, utilization and sequestration (CCS)

Gas separation of carbon dioxide from other gases had been investigated for decades (Choi et al., 2009; Li et al., 2011). In the purification of natural gas, carbon dioxide is removed from methane gas since natural gas reservoir contains large amount of carbon dioxide. It is believed that one-third of carbon dioxide emission had been attributed to the fossil-fuel burning plants, which emit more carbon dioxide than the natural gas purification (Choi et al., 2009).

As the removal of carbon dioxide is a crucial issue nowadays, many works had been proposed. There are three ways to reduce the emission of carbon dioxide to the atmosphere, that are reducing energy intensity, reducing carbon intensity, and improving the carbon dioxide sequestration technique (D'Alessandro et al., 2010). The concept of CCS is roughly illustrated in Figure 2.1 and it is believed that CCS is able to reduce more than 50% of the current CO_2 emission from the CO_2 point sources at reasonable costs (Hasan et al., 2014).

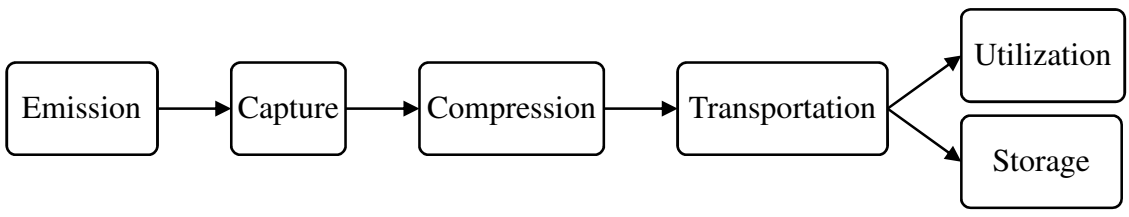

Figure 2.1: Conceptual CCS chain (Hasan et al., 2014).

CCS was introduced to reduce the amount of carbon dioxide released to the atmosphere compare to plant that do not apply CCS (IPCC, 2007). From Figure 2.2, it shows that the amount of carbon dioxide produced in the plants with CCS is much higher than the conventional plants that had been attributed to the extra energy required to capture, compression, transfer and store the carbon dioxide. However, due to the application of CCS system, the amount carbon dioxide released to the atmosphere by the plants with CCS is way lower than the conventional plants.

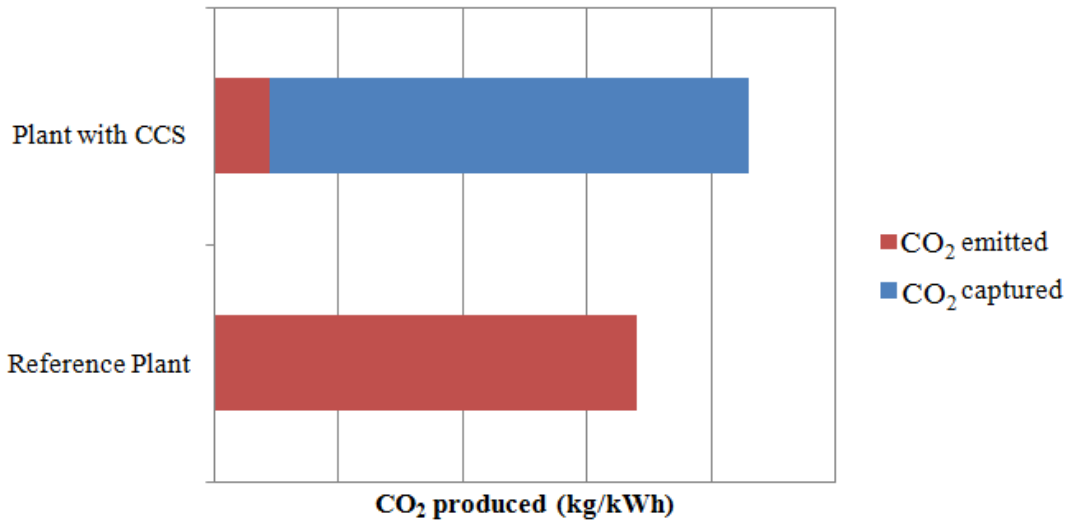

Figure 2.2: Comparison of carbon dioxide emitted and captured by plant with and without CCS (IPCC, 2007).

The main idea of CCS technique is to capture the carbon dioxide, transfer it to a reservoir, and isolate it permanently from the atmosphere. Carbon dioxide capture is more likely to apply on a large point source such as industrial plants rather than on the small and mobile sources such as transportation since this is more cost effective (Choi et al., 2009; D'Alessandro et al., 2010). Carbon dioxide capture systems that had been applied are post-combustion, pre-combustion, and oxy-fuel combustion (Mondal et al., 2012). The differences of these three systems will be described and shown in Figure 2.3.

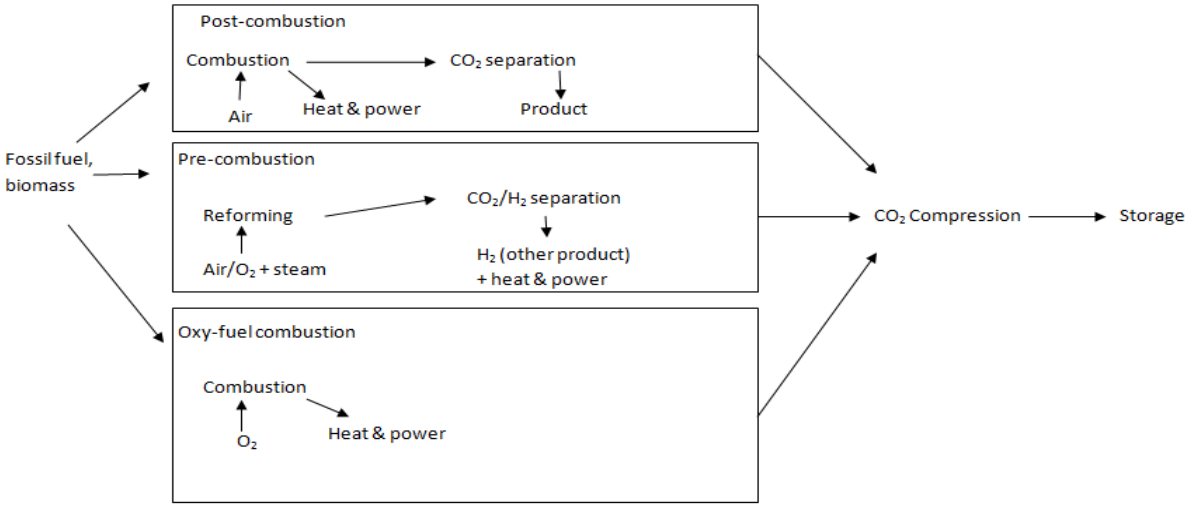

Figure 2.3: Brief schematic representation of capture systems (IPCC, 2007).

Post-combustion involves the capture of carbon dioxide after fossil fuel burning with air, which means the CO_2 is separated from the flue gas containing NO_x and SO_2 (Feron and Hendriks, 2005). In the pre-combustion process, the fuel reacts with air or oxygen to give syngas which is mainly composed by carbon monoxide and hygrogen gas where carbon monoxide will be turned into carbon dioxide and hydrogen (Figueroa et al., 2008). Then, carbon dioxide will be removed while hydrogen will be used as a fuel. The transition of carbon fuel to non-carbon fuel can bring the plant extra products and profits. The oxy-fuel combustion is basically same as the post-combustion system except only pure oxygen is used in oxy-fuel combustion system that will raise the operation cost much higher than the post-combustion system (Pires et al., 2011). The advantages and disadvantages of each CCS systems are listed in Table 2.1.

Table 2.1: Advantages and disadvantages of CCS system (Olajire, 2010; Li et al., 2011).

	Advantages	Disadvantages
Post-combustion	• Applicable for low CO_2 concentration • Easy cooling process • Low CO_2 partial pressure needed • High kinetics performance • Easily retrofit to existing power plant	• Corrosion due to basic solvent • Solvent degradation • Large equipment required • High energy and cost needed for solvent regeneration • Limitation on solvent concentration due to foaming properties and viscosity
Pre-combustion	• Potentially less expensive than post-combustion capture • Low emission • Higher CO_2 concentration and pressure in output compared to post-combustion capture	• Efficiency loss in water-gas shift section • Extra cost for cooling • Extensive supporting system required
Oxy-fuel combustion	• No CO_2 separation is required • Boiler size can be reduced • Potential to lower energy consumption with membranes • Easily retrofit to existing power plant	• Immatured technology • Corrosion of equipment will be increased by increased SO_2 concentration • Combustion of pure oxygen will be relatively difficult • High production cost due to large cryogenic oxygen production • Decreased process efficiency

Among the three options, post-combustion is the most developed technique because it can capture the carbon dioxide from flue gas without significant modification of existing plant and high capital cost (Kenarsari et al., 2013).

2.2 Types of carbon dioxide capture

The separation of CO_2 can be divided into physical and chemical processes, where the most common and developed processes are absorption and adsorption (Feron and Hendriks, 2005; Pires et al., 2011; Goeppert et al., 2012). The CO_2 separation by adsorption and absorption is mentioned and discussed in this section.

2.2.1 Liquid absorption

Absorption is a physical or chemical process that involves the dissolve of atoms, molecules or ions in a bulk phase (Al-Ghawas et al., 1989). So, absorption can be categorized into physical absorption and chemical absorption. A typical chemical absorption consists of an absorber and a stripper while the absorbent is usually regenerated by thermal heating (Feron and Hendriks, 2005; Yang et al., 2008). Chemical absorption involves the forming of chemical bonding between absorber and absorbent. It can be regenerated by thermal heating to break the weakly bonded molecules. Then, the basic solvent can be recycled to the absorption tower and a pure carbon dioxide stream also can be obtained. On the other hand, physical absorption only involves the carbon dioxide physically absorbed on the organic solvent (Yu et al., 2012a).

2.2.1 (a) Chemical absorption

For chemical absorption, Danckwerts (1979) suggested that carbamate will be formed through a zwitterion mechanism if primary or secondary amines are used, as shown in Figure 2.4. One of the conventional ways to capture carbon dioxide from a

large point source that had been commercialized is known as “wet-scrubbing”. This post-combustion wet-scrubbing method had been established in the industry for over 60 years by using monoethanolamine (MEA). The advantage of solvent absorption is the amine can be regenerated by thermal heating and it can be easily fitted to existing plant without significant modification (Lee et al., 2008). However, there are few weaknesses of this capture method that needed to be overcome. First, the residual oxygen remained in the flue stream will associate with the amines to corrode the absorption stream. So, it is necessary to use an inhibitor to prevent the absorption tower from corrosion. Besides that, other gases such as sulfur dioxide and nitrogen dioxide produced during the fuel burning will reduce the efficiency and thus increase the electricity cost (Yang et al., 2008).

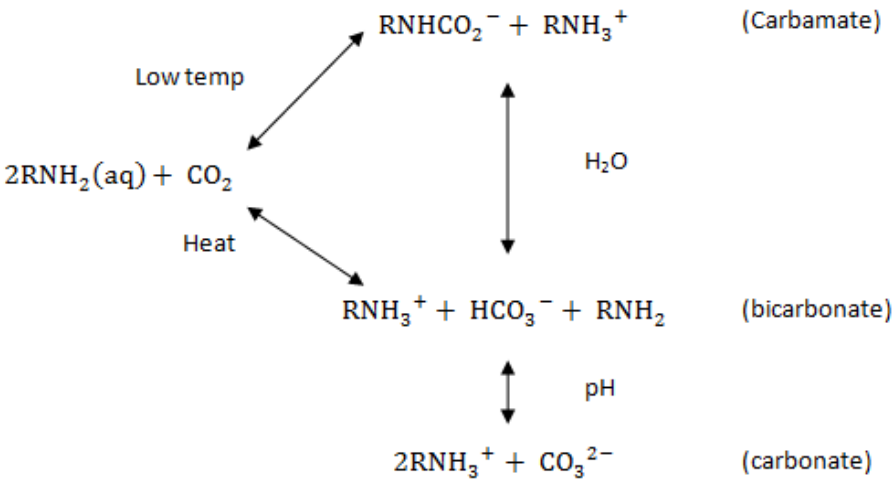

Figure 2.4: Proposed reaction mechanism in liquid amine absorption (Gray et al., 2005).

Donaldson and Nguyen (1980) proposed that tertiary amines do not react directly with carbon dioxide to form stable carbamate. Tertiary amine in this case only serves as a weak base to produce hydroxyl groups (OH^-) to react with carbon dioxide because it doesn’t have the hydrogen atom to be displaced by carbon dioxide

(Sada et al., 1989). Dubois and Thomas (2011) studied the carbon dioxide removal by different amine based aqueous solution. They found that absorption performance for tertiary (*N*-methyldiethanolamine) and sterically hindered amines (2-amino-2-methyl-1-propanol) can be enhanced by addition with activator (piperazine) or MEA.

Gaur et al. (2010) compared the efficiency of carbon dioxide absorption from landfill gas by 2 different alkanoamines, which is MEA and diethanolamine (DEA). In order to obtain more accurate results, they removed other poisonous compounds presented such as carbon tetrachloride, toluene, chloroform, xylene and benzene via physical adsorption by using activated carbon before carbon dioxide removal. The results show that MEA gives better absorption efficiency but worse cyclic capacity than DEA. It is the same for secondary amines that stable carbamates will be formed when react with carbon dioxide.

Instead of alkanoamine, carbonate and water washing process are also applied in the ammonia manufacturing industry to remove CO_2 gas. The most common process is called as Benfield Process that used amine-promoted hot potassium carbonate solution (usually known as Benfield solution) as absorbent (Bartoo, 1984). Yi et al. (2009) investigated the absorption of CO_2 by Benfield solution in rotating packed bed (RPB) and the result shows that RPB has better mass transfer efficiency in the inlet region of the packing.

Ionic liquid (IL) has been widely studied due to its unique properties such as very low vapour pressure, good thermal stability, high polarity and non-toxicity (Bates et al., 2002). IL can be used as CO_2 absorbent either by physical absorption or chemical absorption. Wang et al. (2013) proposed that room temperature ionic liquids (RITLs) can be a substituent for amines due to its properties such as low

vapour pressure, wide liquid range, thermal resistant and tunable properties. RITLs is a potential liquid absorbent to be used because it can be designed according to the industrial environment. It is also thermally and chemically stable that can avoid the problem of corrosion like the conventional amine absorption.

2.2.1 (b) Physical absorption

For physical absorption, there are few physical absorption processes had been employed commercially which are Estasolvan, Selexol, Purisol, Rectisol, Sepesolv-MPE, and Fluor process where the adsorbent used are tributyl phosphate, dimethyl ether of polyethylene glycol, normal methyl pyrrolidone, methanol, mixture of polyethylene glycol dialkyl ethers, and propylene carbonate respectively (Kovvali and Sirkar, 2002). These processes are used to remove acid gas from a gas stream by using solvent with high pressure application. Physical absorption obeys Henry's Law that the amount of gas molecules dissolves in the solvent depends on the pressure and temperature (Olajire, 2010). Carbon dioxide absorption of organic solvent is favoured at the condition with high carbon dioxide partial pressure with low temperature. Thus, the regeneration process can be done by decreasing the pressure or by heating (Yu et al., 2012a).

Although liquid absorption is the most applied technology in power plants, the problems listed in Table 2.2 show that CO_2 absorption by basic solvent such as amine solution show that there is still room for process improvement. For instance, there are many studies had been done on solid adsorption, gas separation membranes, and cryogenic distillation (Yang et al., 2008). Among these three alternatives, gas separation membranes and cryogenic distillation are commercially available while

physical adsorption still under research (Olajire, 2010). Mathias et al. (2013) summarized the desired solvent characteristics that should be considered, which are high capacity and low enthalphy of absorption, high mass transfer and chemical kinetics, cost and availability, low viscosity, low degradation tendency, low volatility, toxicity, and low fouling tendency.

Table 2.2 shows the comparison between liquid and solid sorbents. It also shows that there are many constraints facing in these technologies and lots of research should be carried out to improve existing technologies.

Table 2.2: Comparison between liquid and solid sorbents (Olajire, 2010).

	Advantages	Disadvantages
Liquid absorption	• High reaction rate and high CO_2 absorption capacity • Reusable • Commercially mature • Easily retrofit into existing plant	• Degraded product from solvent is not environmental and human friendly • Low contact area between gas and liquid • High regeneration cost • Corrosion • Work at elevated temperatures (100-140 °C) • Reduce plant efficiencies
Solid adsorption	• Cost and size of boiler can be reduced • Can work under a wide temperature range from ambient temperature to 700 °C • Lower regeneration energy needed • Can be disposed with less environmental issues • Produce less waste when cycling	• Sorbent attrition • Relatively difficult for cooling • Pressure drop in output • Lower adsorption capacity

2.2.2 Solid adsorption

Adsorption can be defined as the accumulation of gases or liquids on the surface of a solid (Brunauer et al., 1938). It involves the attraction of chemical species in gases and liquids to the surface of solids which is the basis of the separation process. The solid is usually known as adsorbent and the component attracted is known as adsorbate. An adsorption isotherm is a plot or equation that relates the equilibrium amount of adsorbates held by a given mass of adsorbent to the adsorbate partial pressure or concentration in the surrounding gas at a specified temperature (Crini and Badot, 2008). The terms *adsorption* and *desorption* are often used to indicate the direction from which the equilibrium states had been approached. There are three main types of adsorption which are ion-exchange, physisorption and chemisorption as described in Table 2.3.

Table 2.3: Description of types of adsorption (Yu et al., 2012a).

Term	Description
Ion exchange	• The exchange of ionic species of adsorbate with ionic species on the adsorbent • Commonly used in waste water treatment to remove metal ions from water resource.
Physisorption	• A reversible process that involves van der Waals interaction between adsorbent and adsorbate • Occur as multilayer at high relative pressure • Exorthemic process but the energy is low
Chemisorption	• A process involves formation of chemical bondings • Only monolayer adsorption occurred • Exorthemic process but the energy is relatively higher

2.2.2 (a) Adsorbent

Adsorption is one of the common processes used in the industries due to the ease of operation, simplicity of design and low regeneration cost. This is because of the absence of chemical bond formation between absorbents and absorbate that may raise the energy needed for absorbate recovery process. According to Yong et al. (2002), an adsorbent must fulfil these properties:

1. High selectivity and adsorption capacity for carbon dioxide at high temperature
2. Adequate adsorption/desorption kinetics for carbon dioxide at operating conditions
3. Thermal, chemical and mechanical stabilities under extensives recycling

Throughout these years, adsorbents such as metal oxide, zeolite, clay, activated carbon, and others had been studied for carbon dioxide capture. Researches on adsorbent mainly aim to develop an adsorbent with low cost raw material, low heat capacity, fast kinetics, high CO_2 adsorption uptakes, high selectivity and high stability under recycling (Choi et al., 2009). The surface properties of adsorbents such as porous structure, pore size distribution, specific surface area, and hydrophilic-hydrophobic properties play important roles in the adsorption capacity (Wang et al., 2011a).

Solid adsorbents can be divided into two groups which are physisorbents and chemisorbents (Brunauer et al., 1938). Physisorbents are temperature-sensitive and have comparatively lower selectivity. The adsorption performance of physisorbent

can be improved by enhancing the surface area and pore structure (Pierotti and Rouquerol, 1985). On the other hand, chemisorbents have relatively higher adsorption capacity and selectivity towards carbon dioxide (Pacchioni, 1993). Nowadays, there are works that try to combine these adsorbents to overcome their weaknesses and thus hybrid materials are widely studied in the application of carbon dioxide adsorption (Choi et al., 2009).

The ability of oxide nanoparticles to adsorb carbon dioxide also had been reported, especially the use of porous inorganic metal oxides such as alkali metal oxide and alkali-earth metal oxides. Baltrusaitis et al. (2011) stated that major adsorption products were bicarbonate, mono- and bidentate carbonates, and the adsorption capacity of oxide nanoparticles may be altered by the presence of co-adsorbed water. Metal-organic frameworks (MOFs) have been investigated as a new nanoporous material that possess well-defined structure, high surface area, desired functionalities, and controllable pore size. Bao et al. (2011) prepared a magnesium-based metal-organic framework which known as Mg-MOF-74 and the carbon dioxide adsorption properties had been studied. They compared the Mg-MOF-74 with zeolite 13X and found that Mg-MOF-74 had higher carbon dioxide adsorption capacity and surface area with a similar CO_2/CH_4 selectivity. Wang et al. (2012b) prepared a layered double hydroxide-derived metal oxide as a carbon dioxide adsorbent that can be used at an intermediate reaction temperature which operates in the temperature of 200-400 °C. They stated that the effect of inter-layer anions used can affect the carbon dioxide adsorption properties of prepared sample due to the micropores formed during decomposition depend on the types of anions used. In general, carbon dioxide adsorption properties of an adsorbent depend on the micropores and surface chemistry. Mohammadi et al. (2014) used eggshells as the

raw material to prepare low cost CaO powder and further incorporated with refractory dopants such as Ti, Al, Cu and Zr. The Zr-doped CaO sorbent showed the best performance, which the conversion of around 88% could be sustained within 20 cycles.

Natural zeolite is a porous hydrated aluminosilicate compound with SiO_4 and AlO_4 molecules built into tetrahedron structure. The distribution of exchangeable cations existed in the channels throughout the structure, zeolite purity, its size and its structure and composition play an important role on its adsorption properties (Wang et al., 2011a). The common zeolites that widely studied in the CO_2/N_2 separation are zeolite X, Y, A, β and chabazite. Araki et al. (2012) synthesized zeolite rho by using 18-crown-6 ether and found that it has higher adsorption capacity and CO_2/N_2 selectivity compared to SAPO-34 and Na-X adsorbents. Su and Lu (2012) tested zeolite 13X reusability for 100 cycles by using a dual column temperature/vacuum swing adsorption (TVSA). They found that energy spent for regeneration is relatively low and zeolite 13X is able to show stable carbon dioxide adsorption performance under humid condition. Silva et al. (2014) studied the sorption of binary mixtures of CO_2 and CH_4 in binderless pellets of zeolite 13X between 313 and 423 K with total pressure up to 5 atm. The adsorption capacities for CO_2 in a equimolar CO_2/CH_4 mixture at 5 atm is 4.6 mmol/g at 303 K. The adsorption capacity for CO_2 is 20% higher than CECA 13X binder pellets Even though zeolite has high surface area and crystalline structure, there are some drawbacks that existed when using zeolite as CO_2 adsorbent. The CO_2 adsorption uptake is relatively low in the system consists of CO_2/N_2 binary system. Besides that, the hydrophilic properties of zeolite will decrease the CO_2 adsorption capacity when there is moisture in the adsorption system. Chen et al. (2014) prepared zeolite 13 X by using bentonite with alkaline